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CHARACTERIZING SURFACE LAYERS IN NITINOL USING X-RAY PHOTOELECTRON SPECTROSCOPY

REBECCA CHRISTOPFEL AND APURVA MEHTA

ABSTRACT

Nitinol is a shape memory alloy whose properties allow for large reversible deformations and a return to its original geometry. This nickel-titanium (NiTi) alloy has become a material used widely in the biomedical field as a stent to open up collapsed arteries. Both ambient and biological conditions cause surface oxidation in these devices which in turn change its biocompatibility. The thickness of oxidized layers can cause fractures in the material if too large and can allow for penetration if too thin. Depending on the type and abundance of the chemical species on or near the surface, highly toxic metal ions can leak into the body causing cell damage or even cell death. Thus, biocompatibility of such devices is crucial. By using highly surface sensitive x-ray photoelectron spectroscopy to probe the surface of these structures, it is possible to decipher both layer composition and layer thickness. Two samples, both of which were mechanically polished, were investigated. Of the two samples, one was then exposed to a phosphate buffered saline (PBS) solution to mimic the chemical properties of blood, while the other remained unexposed. Although both samples were found to have oxide layers of appropriate thickness (on the order of a few nm), it was found that the sample exposed to the saline solution had a slightly thicker oxide layer and more significantly, a phosphate layer very near the surface suggesting toxic metal components are well contained within the sample. These are considerable indications of a biocompatible device.

INTRODUCTION

The equiatomic nickel-titanium alloy (Nitinol) is an advanced material, increasingly used as a biomedical device [4]. It is critical that a foreign body implant is biocompatible. Understanding the nature of the surface oxide layers on these devices helps determine the biocompatibility and, consequently, the usability of such materials. Biocompatibility is “the ability of a material to perform with an appropriate host response in a specific application” [1]. A device under investigation is tested both *in vitro* and *in vivo* to examine the degree of toxicity of the devices to cells of the material. Materials that are not biocompatible induce many complications in the body. Specifically, corrosion of metals can create toxic metal ions inducing cell damage [2]. In the case of Nitinol, nickel and nickel compounds are the components that are at the center of toxicity concerns.

In this experiment the NiTi alloy tested is used to manufacture stents to open collapsed arteries. Several different alloys whose production processes vary are being tested to better understand the surface oxidation that occurs and what affects such oxidation can have when implanted.

By probing the surface of these metallic structures it is possible to determine the composition and layer formation of the samples under investigation. The comparison of titanium vs. titanium oxide and nickel vs. nickel oxide can be used to determine abundance and location of species within a sample. The technique used is x-ray photoelectron spectroscopy (XPS), a highly surface sensitive, non-destructive method which involves irradiating a material with x-rays while measuring the kinetic energy and number of emitted photoelectrons. The binding energy of the core electron is then determined as the difference between the incident x-ray energy and the kinetic energy of the photoelectron. Analyzing the position and intensity of spectrum allows determination of the amount of different chemical species in the material. Escape depth of electrons from a material is very small: ~1–2 nm and is strongly dependent on the kinetic energy, therefore by varying the energy of the incident photon (and thus the kinetic energy) and/or changing the angle of incidence, it is possible to determine the location of the identified species as a function of depth from the surface. This technique is used to understand the character of the oxidation/corrosion layer on NiTi when exposed to different chemical environments including a liquid that mimics the chemical properties of blood. This technique

is also unique in its tunability of incident x-ray beams, allowing for a specific range of energies to be examined. Moreover, by changing the sample/detector orientation it is possible to identify depths of species within a sample. Compared to other surface analysis techniques that offer structural information about a sample, XPS allows for a determination of the atomic compositions of a sample or the chemical state of a certain element, as well as a comparative depth analysis.

MATERIALS AND METHODS

The samples of interest in this experiment include two different Nitinol substrates. Nitinol is a shape memory alloy (SMA). If it undergoes some deformation from its original crystalline structure, it has the ability to regain its original geometry when heated or cooled. The property that enables such processes is the superelasticity of a material, the amount of strain a material can handle before the atomic structure is permanently altered.

Both samples were mechanically polished, a process that strips away surface materials. This was followed by cleaning with acetone and then distilled water in an ultrasonically agitated bath to ensure a clean, uncontaminated surface [3]. One of the samples was then soaked in a simulated biological fluid known as phosphate-buffered saline (PBS) that consists of 0.154 M NaCl, 0.0003 M Na₂HPO₄ and 0.004 M KH₂PO₄ (pH 7.4), and PBS with an addition of 0.0013 M CaCl₂ [4]. This solution acts as a liquid that mimics the chemical properties of blood, enabling a determination of the biocompatibility of such devices. The other sample has not exposed to the saline solution.

Measurements were carried out at beam line 5-1 at Stanford Synchrotron Radiation Laboratory (SSRL), a station designed to carry out the specific needs of XPS. The end-station is equipped with two interconnecting ultra high vacuum chambers with operation pressure in the low 10⁻¹¹ Torr range. One chamber is dedicated to surface preparation and contains an ion gun for ample sputtering, mass spectrometer for residual gas analysis and thermal desorption spectroscopy (TDS), pulsed gas dosing system and low-energy electron diffraction (LEED) optics. The other chamber, dedicated to core level spectroscopy, houses a hemispherical SES-100 electron analyzer (VG-Scienta) and a multi-channel plate partial electron yield detector as well as a collimated beam gas-doser regulated by the backing pressure at the backside of an array of multi-channel plates.

The sample rod allows the mounting of several different samples at the same time, each having a grazing incident angle of the photon beam to the sample of about 5° or less. The sample rod can be rotated around the photon beam axis allowing for variation of the escape angle of the electron and therefore variation of escape depth. The manipulator onto which the sample rod is attached is equipped with computer controlled stepper motors for easy alignment in the spectroscopy chamber and transport between the two chambers [4].

Samples were irradiated with x-rays at a known energy of approximately 1,080 eV. For the Nitinol samples under investigation, this incident energy is sufficient to excite different core electrons of interest, that is, titanium, nickel, oxygen and phosphorus. The

detector and sample orientation were varied to provide information about the structure and chemistry of the sample, namely species identification and depth of the various surface elements. The rod and affixed sample were rotated such that the detector was at 0, 18, 48, 60 and 70 degrees from the surface normal of the sample.

An overview scan was taken at the beginning of each of the detector/sample orientations to ensure an appropriate scan range of the different species. Knowing the binding energies of a particular elemental core electron and thus their specific kinetic energies, a spectrum was then obtained to show peaks in a particular range. The Ni3p electron has binding energies of 68 and 66.2 eV due to spin-orbit splitting, while the Ti3s electron has a binding energy of 58.7 eV and thus showed peaks in the kinetic energy range of approximately 1,015 eV and 1,025 eV, respectively. See Figure 2. Each species and associated core electrons were subject to smaller range scans such that each peak with a specific energy was well defined. This was done at each of the five detector/sample orientations in six different energy ranges. Depending on the resolution of the spectrum, each energy range was swept by the x-ray beam for a certain number of frames, whereby the length of the sample is scanned by the beam, and the intensity of each spectra are summed. Final intensities and corresponding kinetic energies are recorded. See Figure 1. This was done separately to both the sample exposed to the saline solution and the sample left unexposed.

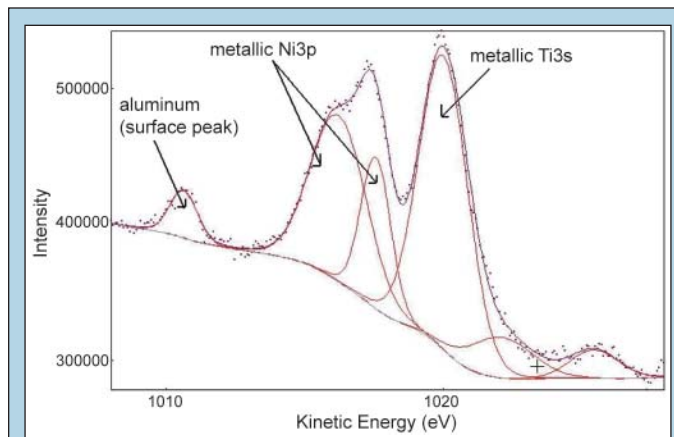


Figure 2. Example of curve fitting and labeled peaks for mechanically polished spectra at 60 degrees. This shows ejected electrons with kinetic energies of 1,010–1,025 eV. Species of interest are aluminum, nickel and titanium. Dotted line indicates data; solid line indicates fit.

To come up with a physical model of the speciation and location of said species that exist on the surface of Nitinol, a theoretical model is first called upon. To excite core electrons, sufficient incident energy is required. The intensity of photoelectrons collected by the detector then becomes a function of this incident photon flux, and the combination of parameters associated with the irradiated material as well as the detector position and geometry. Thus, an equation for number of counts from a given signal, S , for a given layer of finite thickness is given by an adapted equation for measuring counts in a given spectra [8].

$$S(\alpha, \beta) = I_0 \left[e^{-\frac{\mu d}{\cos \beta}} \left(-\frac{h}{\cos \beta} \right) Df \right] e^{-\frac{d}{\lambda \cos \alpha}} Gt \quad (1)$$

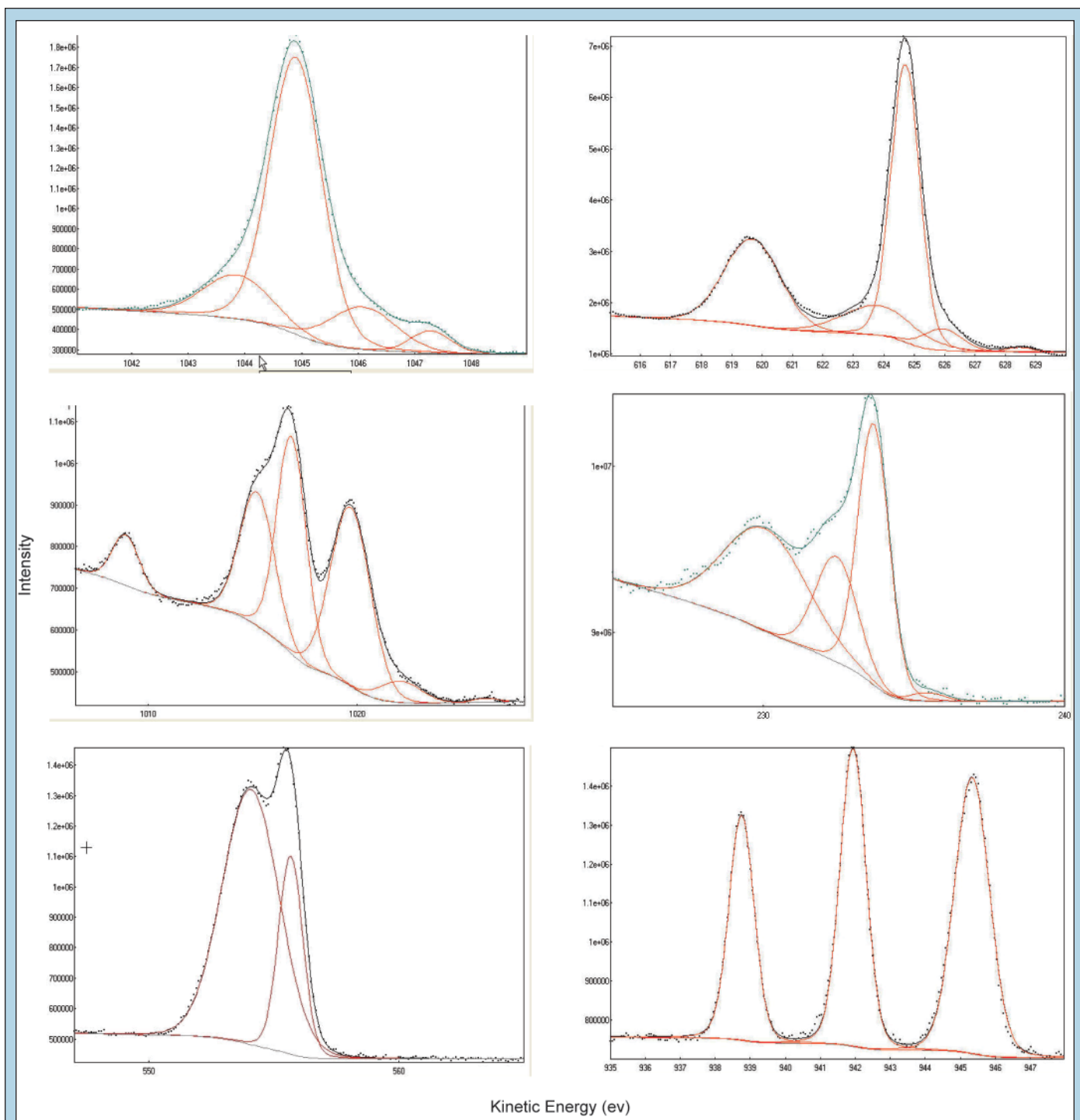


Figure 1. Spectra and fitted peaks for the six small range energy scans. These energy ranges include core electrons of interest: Ti3p, Ti2p, Ni3p, Ni2p, O1s and P2p from left to right, top to bottom. Dotted lines indicate data; solid lines indicate fits.

Where α = angle of detector with respect to surface normal of sample (in degrees), β = angle of incident x-ray (in degrees), I_0 = intensity ($\text{W} \cdot \text{m}^{-2}$), μ_x = property of incident x-ray traveling through material which depends on energy of photon and material (m^{-1}), d = depth (m), h = width of area probed by x-ray (m), D = concentration of species, f = rate at which electrons are ejected from sample (cross section), λ = function of material that depends on KE

of electron and material in which it propagates (m), G = detector geometry and t = time (s).

Under some constraints and by making some assumptions [6], a signal to signal ratio of peaks whose energies are very close allows for elimination of many of the unknowns and can provide a qualitative model of the structure by locating surface and near surface layers with respect to one another.

$$\frac{S_1}{S_2} = C e^{-\frac{1}{\lambda \cos \alpha} (d_1 - d_2)} \quad (2)$$

where C is a collection of constants and parameters whose values do not depend on detector angle α while d_1 and d_2 are depths of a certain species from the surface of the sample. By taking the natural log of Eq. (2) we get a linear relationship where the natural log of the signal ratio is inversely related to $\cos \alpha$.

$$\ln\left(\frac{S_1}{S_2}\right) = \ln(C) - \frac{1}{\cos \alpha} \left(\frac{d_1 - d_2}{\lambda}\right) \quad (3)$$

The line has a y-intercept equal to $\ln(C)$ and a slope equal to $-\left(\frac{d_1 - d_2}{\lambda}\right)$. Thus, when the natural log of the signal ratio is plotted against $\frac{1}{\cos \alpha}$, the length $d_1 - d_2$ can be calculated and the distance between two different species in a sample is estimated. The value for λ , the inelastic mean free path of electrons in a sample, is known and assumed to be the same for species whose energies are very close.

RESULTS AND DISCUSSION

Once plotted, information regarding depth and abundance of species was determined. A large positive slope implies that the depth of species relative to the surface species is very deep, while a small positive slope implies a species closer to the reference species, but still below it. A negative slope implies a species above the reference. If we pick a reference species, say alumina, which we assume is remnant from the mechanical polishing and therefore very near the surface and determine the depth of the other layers with respect to that, we can get a reasonable picture of the composition of surface layers.

Theory tells us that purely metallic peaks occur at lower binding energies and will therefore have higher kinetic energies. Oxidized peaks, whose valence electrons are paired with an oxygen molecule, have more tightly bound core electrons and thus a higher binding energy. The signals used to come up with the relevant signal-to-signal ratio are the areas under the fitted curves of the plotted spectrum. The peaks were fit with a series of curves which had a small and fixed amount of Lorentzian component and a large variable Gaussian component. The widths, energies and areas under the various peaks in the specific energy range of the P2p electron are listed in Table 1 and show the data acquired at various angles. Data shows multiple peaks for a given core level and therefore imply surface layers contain species with various oxidation levels, including the stable oxidation states of titanium oxide, TiO_2 and nickel oxide, NiO , as well as partially oxidized nickel peaks. The number of peaks becomes evident in the fitting process; however the identification of all peaks has not been possible. Further investigation and an alternative experimental approach is needed for completion. To come up with helpful information regarding the structure of these two samples, specific signal to signal ratios were taken, metallic peak to a sum of the oxidized peaks — or more generally, a reference peak to a series of other peaks, at multiple angles. See Figure 2 for an example of a spectrum and labeled peaks. Lines are fit to the data points and structural information about the composition of the mechanically polished sample and the mechanically polished sample exposed to the PBS solution is revealed. Comparisons between samples can then be made.

Phosphorus (P2p)–MPPBS	Peak 1	Peak 2	Peak 3
Angle			
	AREA		
0 deg	5.46E+05	7.48E+05	9.16E+05
18 deg	5.79E+05	7.79E+05	9.79E+05
48 deg	3.33E+05	4.48E+05	6.88E+05
60 deg	2.01E+05	2.73E+05	5.18E+05
70 deg	91258	1.28E+05	3.48E+05
	ENERGY		
0 deg	938.7615	941.9441	945.3409
18 deg	938.8604	942.0377	945.4329
48 deg	938.8463	942.03	945.4292
60 deg	938.765	941.9416	945.3619
70 deg	938.753	941.9194	945.3792
	GAUSS		
0 deg	0.7627	0.7926	1.092
18 deg	0.7777	0.7951	1.087
48 deg	0.7661	0.7834	1.09
60 deg	0.7554	0.7894	1.064
70 deg	0.7637	0.7843	1.075

Table 1. Sample of data collected from P2p electron energy range for the sample exposed to the PBS solution, including area under various peaks, energy, and Gaussian width.

By analyzing the slopes of these lines from a series of different spectra it is possible to formulate a layer-by-layer model of each of the samples without necessarily knowing the composition of each layer or the arrangement of the constituents between layers. Regardless, an understanding of the configuration of oxide layers can help determine the biocompatibility of these devices. The plot of $\ln\left(\frac{S_1}{S_2}\right)$ vs. $\frac{1}{\cos \alpha}$ yields lines whose slopes are indicative of depth from surface or separation distance from that of another species. In Figures 3 and 4, linear fits and R^2 values are shown from both the

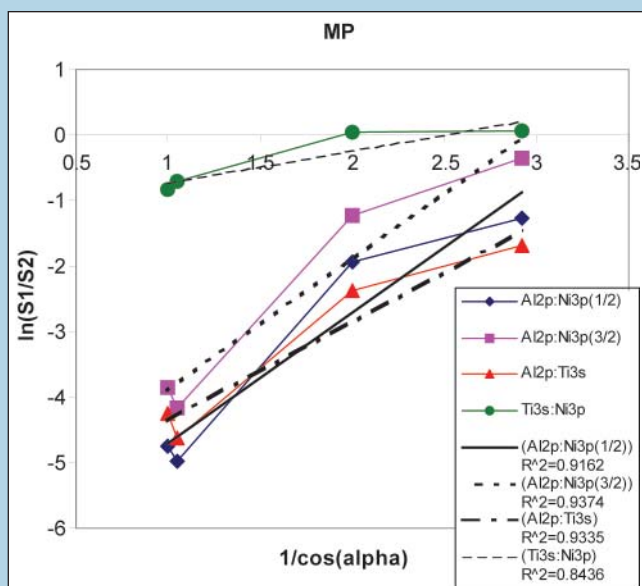


Figure 3. Plots, best fit lines and R^2 values for the mechanically polished sample. Signal to signal ratios were taken of the spectrum whose energy range spans electrons ejected with kinetic energies of 1,010–1,025 eV as detector/sample orientation was rotated through a series of angles.

mechanically polished sample and the mechanically polished sample exposed to solution over several angles in a particular energy range. The results from these plots (as well as all others not shown) are presented in Table 2. Using the surface aluminum signal and that of the metallic nickel signal(s), a surface to substrate depth can be calculated. Since the slopes of these lines are positive, it is clear that the nickel lies beneath the aluminum. See Table 2. Similar depth analyses were done between all relevant signals to build a layer-by-layer model. See Figure 6.

The mechanically polished (MP) sample appears to have a thicker oxide layer than that of the mechanically polished sample exposed to the PBS solution (MPPBS). However, the different forms of nickel oxides are further from the bulk material suggesting they are closer to the surface in the unexposed mechanically polished sample. The mechanically polished sample and the mechanically polished sample in PBS solution have an approximate 5 nm surface-to-substrate thickness. This was determined by comparing the surface aluminum signal to that of metallic titanium whose depth is associated with that of the Nitinol substrate. In both samples, the majority of the 5 nm thickness was titanium oxide, with some metallic nickel and nickel oxide very near the base of this titanium oxide. In addition, the PBS exposed sample included a thin layer of oxidized phosphorus near the surface.

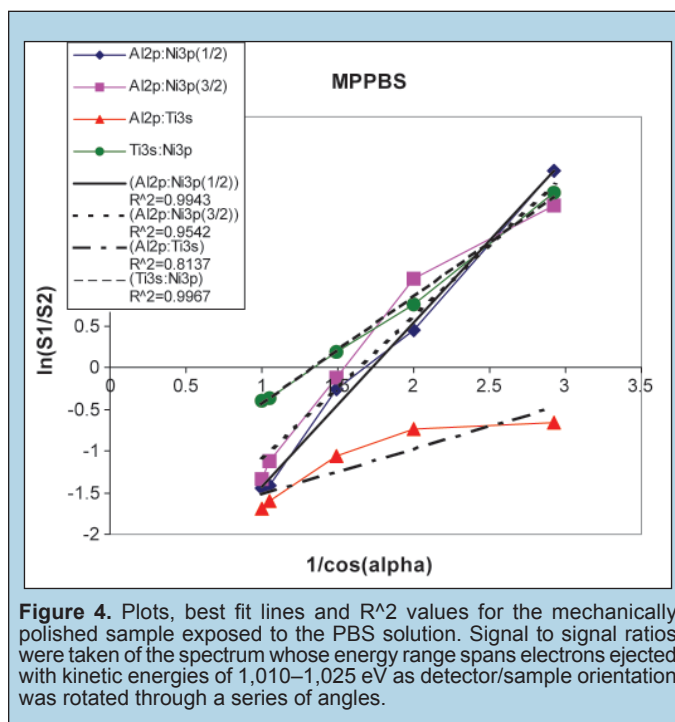
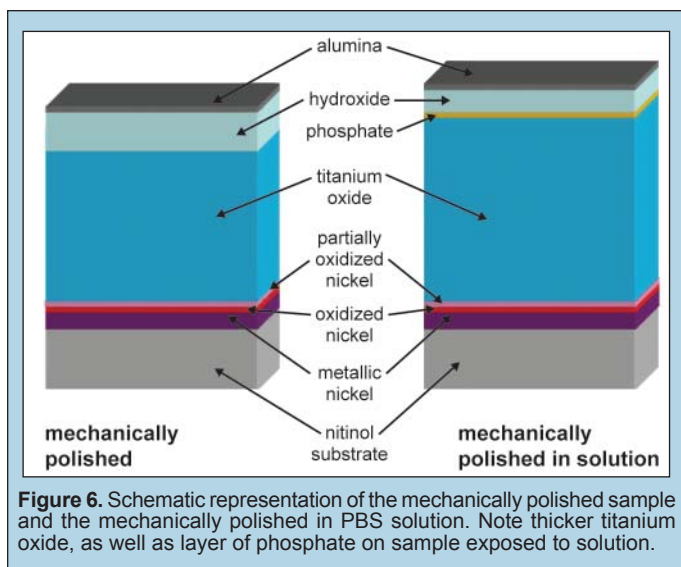


Figure 4. Plots, best fit lines and R^2 values for the mechanically polished sample exposed to the PBS solution. Signal to signal ratios were taken of the spectrum whose energy range spans electrons ejected with kinetic energies of 1,010–1,025 eV as detector/sample orientation was rotated through a series of angles.

	MP	MPPBS	KE (avg.)	Lambda (nm)	Thickness (MP)	Thickness (MPPBS)
Ni3p						
Al2p:Ni3p(1/2)	1.9943	1.9701	1020	2	3.9886	3.9402
Al2p:Ni3p(3/2)	2.0072	1.7247	1020	2	4.0144	3.4494
Al2p:Ti3s	1.5122	0.5418	1020	2	3.0244	1.0836
Ti3s:Ni3p	0.4856	1.2927	1020	2	0.9712	2.5854
Ni2p						
metallic:partially	-0.6162	4.3377	233	0.8	-0.49296	3.47016
metallic:oxidized	-0.4214	-2.4838	233	0.8	-0.33712	-1.98704
partially:oxidized	0.1949	-6.8217	233	0.8	0.15592	-5.45736
Ti3p						
metallic:oxide	-0.6549	-1.8966	1047	2	-1.3098	-3.7932
Ti2p					0	
metallic:oxide	-0.1296	-0.5714	626	1.4	-0.18144	-0.79996
O1s						
oxide:hydroxide	0.5425	1.0021	555	1.2	0.651	1.20252
P2p						
p2:p0		0.431	950	1.8		0.7758
p2:p1		0.415	950	1.8		0.747
p1:p0		0.016	950	1.8		0.0288
TiO:p2		-0.549		1.9		-1.0431

Table 2. Column 1 (far left) describes which signal-to-signal ratio that was taken. Columns 2 and 3 give the slope of the best-fit line. Lambda is the inelastic mean free path of the electron. The product of the slope and lambda yields thickness separation between said species in nanometers. MP is the sample mechanically polished while MPPBS is the sample mechanically polished and exposed to the PBS solution. Note the MP sample (without solution) shows no phosphorus. Positive slope implies the species foremost in the ratio given in Column 1 lies above. A negative slope implies the species foremost in the ratio given in Column 1 lies below.



CONCLUSION

From quantitative analysis, the data shows oxidation layers of sufficient thickness to prevent harmful nickel ions from leaking into the body. However the sample that was treated with the PBS solution appeared to have a slightly thicker titanium oxide layer and also included phosphorus and phosphate layers near the surface, but below the alumina. An exciting conclusion from this analysis is the fact that the phosphorus lies above the oxide very near the surface. This implies that the potentially harmful nickel and nickel-oxide ions are well contained within the sample exposed to the PBS solution. Moreover, the sample left unexposed experienced less oxidation suggesting that merely by placing such a device in the body allows for slightly thicker oxide layers, leaving the harmful components impenetrable by the phosphate layer. Thus, when exposed to bodily fluids, Nitinol devices improve their biocompatibility.

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